

## A vapour depositing method and an apparatus therefor.

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### Abstract

A vapor deposition apparatus and method in which pulse waveform light is applied to a sample sealed in a reaction chamber. The sample is exposed to gaseous material while the pulse waveform light is applied creating one or plural atomic layers. Alternate layers of plural substances or alternate multiple layers of plural substances can be formed by alternating the introduction of gaseous materials with the application of pulse waveform light.

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## Description

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

The present invention relates to a vapor deposition method for producing a film in the form of an atomic layer or in the form of plural atomic layers on a sample, for example a monocrystal silicon wafer in a reaction chamber by supplying gaseous material to be deposited on the sample and an apparatus therefor.

#### 2. Description of the Prior Art

There is a conventional vapor depositing method in which gaseous material flows from a gas source into a reaction chamber, while a sample in the reaction chamber is heated by a high frequency heater, thereby a CVD film is deposited on the sample. In such a method, since adsorption and reaction take place continuously on the surface of the sample, it is very difficult to produce a film in the form of an atomic layer or in the form of plural atomic layers.

Heretofore, in vapor deposition of a film in the form of an atomic layer or in the form of plural atomic layers, a compound semiconductor was used as the objective material. For example producing of a GaAs layer in the form of an atomic layer or the form of plural atomic layers is carried out by utilizing the characteristic of As that As is not deposited on As.

Further there is a method in which gaseous material is adsorbed by a sample, and thereafter gaseous material in a vapor phase is exhausted, and then the adsorbed substance is decomposed and reacted by the application of light to the sample, and series of the above-mentioned processes are repeated.

However, in the former method, deposition of an elemental semiconductor such as Si and Ge is impossible. On the other hand, in the latter method, producing of a film in the form of an atomic layer or in the form of plural atomic layers is possible when using organic or halogen gas as the gaseous material. However, in the latter method, when hydride is used as a gaseous material, there is the problem that when exhaust gas material in a vapor phase is exhausted, the adsorbed substance is away from the surface of the sample.

## BRIEF SUMMARY OF THE INVENTION

It is one object of the present invention to provide a vapor depositing method for producing a film in the form of an atomic layer or in the form of plural atomic layers in which in the surface of a layer of gaseous material, the adsorption of gaseous material and the decomposition and reaction of adsorbed substance separately occur, and it is possible to instantaneously decompose and react the adsorbed substance by light after the adsorption of gaseous material on the surface of the sample.

It is another object of the present invention to provide an apparatus for the above-mentioned vapor deposition method for producing a film in the form of an atomic layer.

The first object is achieved by a vapor depositing method comprising placing a sample in a reaction chamber, and exposing the sample to gaseous materials introduced into the reaction chamber from a gas source while applying light of a pulse waveform from an source of light of the pulse waveform to the sample, by which a film in the form of of an atomic layer or in the form of plural atomic layers is produced with every application of light of the pulse waveform to the sample. In the present invention, the phenomenon utilized is that time is required for completing the neat adsorption of gaseous material on the sample after the first adsorption of gaseous material on the sample and the decomposition and reaction of the adsorbed substance.

Further the second object of the present invention is achieved by an apparatus comprising a reaction chamber receiving a sample, a gas source from which gaseous material is sent into the reaction chamber, and a source of light of a pulse waveform from which light is applied to the surface of the sample in the reaction chamber through a transparent window of the reaction chamber.

According to the present invention, producing of a film in the form of an atomic layer or in the form of plural atomic layers by applying light to the sample in the reaction chamber from a source of the light of pulse waveform while introducing gaseous material from a gas source into the reaction chamber and exposing the sample in the reaction chamber to the gaseous material: after adsorption of the gaseous material on the surface of the sample, the adsorbed substance can be instantaneously decomposed and reacted by light of the pulse waveform so that a film in the form of an atomic layer or in the form of plural atomic layers is produced on the sample.

## BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings,

Fig. 1 is a schematic representation of an example of an apparatus according to the present invention,  
 Fig. 2 graphically shows an example procedure for depositing germanium on a wafer, when the light from a xenon lamp is repeatedly applied to the surface of the wafer,

Fig. 3 is a graphical representation of variation of thickness (ANGSTROM) of deposited germanium on a monocrystal silicon wafer per pulse relative to wafer temperature (DEG C), wherein the dependence of the thickness of deposited germanium on the wafer per one pulse on the wafer temperature is represented, when light from a xenon flash lamp is repeatedly applied to the surface of the wafer,

Fig. 4 is a graphical representation of variation of thickness (ANGSTROM) of deposited germanium on a monocrystal silicon wafer per pulse relative to partial pressure (Pa) of germanic gas inside the reaction chamber, wherein the dependency of the thickness of deposited germanium on the wafer per pulse on the partial pressure (Pa) of germanic gas inside the reaction chamber is represented, when light from a xenon flash lamp is repeatedly applied to the surface of the wafer,

Fig. 5 is a graphical representation of variation of thickness (ANGSTROM) of deposited germanium on a monocrystal silicon wafer per pulse relative to the pulse interval (sec.), wherein the dependency of the thickness of deposited germanium on the wafer per pulse on the pulse interval is represented, when light from a xenon flash lamp is repeatedly applied to the surface of the wafer,

Fig. 6 is a graphical representation of variation of thickness of deposited germanium on a monocrystal silicon wafer per pulse (ANGSTROM) with a lattice type wafer, wherein the dependency of the thickness of deposited germanium on the wafer per pulse on the lattice type wafer is represented, when light from a xenon flash lamp is repeatedly applied to the surface of monocrystal silicon wafer,

Fig. 7 graphically shows an example procedure for forming a multiautomic layered film including an alternately superimposed layer of substance B on a layer of substance B on a wafer comprising the alternate introduction of gaseous materials A and B into the reaction chamber and the application of light from a xenon flash lamp to the wafer once per introduction of respective gaseous materials A and B into the reaction chamber by which a multiautomic layered film including alternately superimposed layer of substance B on layer of substance B is formed,

Fig. 8 is a sectional view of the multiautomiclayered film formed on a wafer according to the procedure graphically shown in Fig. 7,

Fig. 9 graphically shows an example procedure for forming a film including three alternately superimposed layers of substance B on three layers of substance B on a wafer comprising alternate introduction of gaseous materials A and B into the reaction chamber and the application of the light of xenon flash lamp to the wafer three times per introduction term of respective gaseous materials A and B into the reaction chamber by which a multiautomic layered film including alternately superimposed layers of substance B on layers of substance B is formed,

Fig. 10 is a sectional view of the multiautomic layered film formed on a wafer according the procedure shown in Fig. 9,

Fig. 11 graphically shows an example procedure for forming a film including three alternately superimposed layers of substance B on three layers of substance B on a wafer comprising alternate introduction of gaseous materials A and B into the reaction chamber, the application of light from a xenon flash lamp to the wafer three times per introduction term of respective gaseous materials A and B into the reaction chamber, and changing wafer temperature in association with the introduction terms of respective gaseous material A and B by which a multiautomic layered film including alternately superimposed layers of substance B on layers of substance B is formed,

Fig. 12 is a sectional view of the multiautomiclayered film formed on a wafer according the procedure shown in Fig. 11,

Fig. 13 graphically shows an example procedure for forming a film including three alternately superimposed layers of substance B on three layers of substance B on a wafer comprising forming a layer of substance A according to conventional vapor deposition without applying light from a pulse waveform to the wafer and forming plural layers of substance B on the layer of substance A while applying light from a pulse waveform to the wafer according to the present invention, and

Fig. 14 is a sectional view of the multiautomic layered film formed on a wafer according the procedure shown in Fig. 13.

## DETAILED DESCRIPTION

Referring to Fig. 1, an apparatus according to the present invention comprises reaction chamber 1, reserve

chamber 3 communicating with reaction chamber 1 through door 2 of reaction chamber 1, reaction chamber evacuating device 4, reserve chamber evacuating device 5, gas source 6 for supplying gaseous material to reaction chamber 1 and to reserve chamber 3, and a flash lamp 9 for applying light from flash lamp 9 to the surface of sample 7 in reaction chamber 1 through transparent window 8.

The apparatus according to the present invention further comprises sample stand 10, working coil chamber 11 for supplementary heating of sample 7, said working coil chamber 11 being provided underneath sample stand 10. High frequency oscillator 13 supplies high frequency to working coil 12 provided in working coil chamber 11. Sample conveyor 15 conveys sample 7 to reaction chamber 1, said sample conveyor 15 being provided in reserve chamber 3. Sample 7 is carried through door 16 into reserve chamber 3, and control unit 18 controls the application of light from the flash lamp to sample 7 in association with the introduction of gaseous material into reaction chamber 1. Reaction chamber 1 is provided with a pressure meter 17.

In the following a method for producing a film in the form of an atomic layer or in the form of plural atomic layers by using the above-mentioned apparatus according to the present invention is explained. The formation of a film is carried out by the following procedure: (1) reaction chamber 1 and working coil chamber 11 are evacuated by reaction chamber evacuating device 4 and working coil evacuating device 14, respectively, (2) thereafter carrier gas such as hydrogen is supplied to reaction chamber 1 which has been evacuated from gas source 6, (3) reserve chamber 3 is filled with inert gas such as nitrogen to atmospheric pressure, then the door 16 of reserve chamber 3 is opened, and after the sample is placed on sample conveyor 15 in reserve chamber 3, door 16 is shut, (4) reserve chamber 3 is evacuated by reserve chamber evacuating device 5 to a reduced pressure, while the same gas as the gas supplied to reaction chamber 1 is supplied to reserve chamber 3, (5) the door 2 of reaction chamber 1 is opened, and sample 7 is carried from reserve chamber 3 into reaction chamber 1 by sample conveyor 15, placed on sample stand 10, sample conveyor 15 is returned to reserve chamber 3, and door 2 is shut, (6) high frequency is applied to working coil 12 from high frequency oscillator 13, thereby sample stand 10 is heated, heating sample 7, wherein heating of sample 7 is carried out with a view to promoting decomposition and reaction of gaseous material under application of light from a flash lamp, or with a view to separating an unnecessary adsorbed substance on the surface of sample 7, and with a view to forming a film by a conventional chemical vapor depositing method, (7) thereafter gaseous material is supplied from gas source 6 to reaction chamber 1, and (8) after the time required for adsorbing gaseous materials on the surface of sample 7, light from a flash lamp is applied from flash lamp 9 to the surface of sample 7 through transparent window 8.

In the method according to the present invention, the application of light from flash lamp 9 to the sample is controlled in association with the flow of gaseous material into reaction chamber 1 by control unit 18, and plural kinds of gaseous materials can flow into reaction chamber 1 at the same time or alternately. Further, after applying light from flash lamp 9 to sample 7 while one gaseous material flows into reaction chamber 1, another gaseous material flows into reaction chamber 1, and then by heating sample 7, different substances can be deposited on sample 7.

Fig. 2 is a graphical representation of a time schedule for the application of pulse waveform light to a monocrystal silicon wafer and the introduction of germanic gas into the reaction chamber, together with the output of the pulse waveform light, flow of germanic gas, flow of carrier gas, and change of wafer temperature with time, wherein there is represented an example of a procedure for depositing germanium on a wafer, when the light from a xenon lamp is repeatedly applied to the surface of the wafer.

Referring to Fig. 2, one example procedure when forming germanium for example on a monocrystal silicon wafer is explained. Hydrogen gas 200cc/min flows into reaction chamber 1. When the pressure inside reaction chamber 1 reaches 270 Pa, the monocrystal silicon wafer (sample 7) is placed on sample stand 10, heated to a wafer temperature TG between 230 DEG C and 290 DEG C at time t, further heated to temperature TD of more than 400 DEG C so that unnecessary material adsorbed on the surface of wafer is removed, and thereafter cooled to a wafer temperature TG.

Then, germanic gas ( $\text{GeH}_4$ ) is introduced into reaction chamber 1 at time t so that the partial pressure reaches 1-20 Pa, and after the lapse of timer  $\tau_G$  required for the germanic gas to be adsorbed on the sample 7 in which  $\tau_G$  designates the repeated pulse interval of the light of pulse waveform, light from a xenon flash lamp with 20J/cm is repeatedly applied to the surface of monocrystal silicon wafer at time t1.

According to the above-mentioned method, the thickness of germanium film deposited on sample 7 per

pulse is investigated. When the total pressure of GeH<sub>4</sub>-H<sub>2</sub> gas mixture is 280 Pa, the partial pressure of germanic gas (GeH<sub>4</sub>) is 13 Pa, and the pulse interval  $\tau$  is 20 seconds, the deposition of one atomic layer of germanium per pulse is recognized on Si of lattice type (1 0 0) and Si of lattice type (1 1 1), respectively, at a temperature between 260 DEG C and 275 DEG C without depending upon temperature as shown in Fig. 3, in which  $\delta$  designates the thickness of germanium deposited on Si of the lattice type (1 1 1) per pulse,  $\delta'$  designates the thickness of germanium deposited on Si of the lattice type (1 0 0), and a broken line "a" designates the thickness of one atomic layer of Ge of lattice type (1 1 1) with a wafer temperature, and broken line "b" designates the change of the thickness of one atomic layer of Ge of the lattice type (1 0 0). The same applies to Figs. 4-5.

When the total pressure of GeH<sub>4</sub>-H<sub>2</sub> gas mixture is 280 Pa, and the wafer temperature is 268 DEG C, it is recognized that at a partial germanic gas pressure of more than 13 Pa, germanium of one atomic layer per pulse is deposited as shown in Fig. 4.

When the total pressure of GeH<sub>4</sub>-H<sub>2</sub> gas mixture is 280 Pa, and the wafer temperature is 268 DEG C, it is recognized also that at a partial germanic gas pressure of 4.5 Pa, germanium of one atomic layer per pulse is deposited when pulse interval is long as shown in Fig. 5.

However at a temperature between 230 DEG C and 290 DEG C, when light from flash lamp 9 is applied to sample 7, deposition of germanium is recognized. When the lattice type of wafer is changed, deposition of one atomic layer per pulse of germanium corresponding to the respective lattice type is recognized.

As above-mentioned, it is apparent that the application of pulse waveform light to sample 7 while exposing sample 7 to gaseous material makes it possible to form a of one atomic layer of germanium per pulse. Further, it is well known that formation of one atomic layer of mixed crystal is possible by a flow of material gas mixture including material gases of more than two kinds at the same time into reaction chamber 1.

Fig. 7 is a graphical representation of a time schedule for the application of pulse waveform light to a monocrystal silicon wafer, the introduction of gaseous material A into the reaction chamber, and the introduction of gaseous material B into the reaction chamber, together with an output of pulse waveform light, flow of gaseous material A, flow of gaseous material B, and change of the wafer temperature with time. The graph illustrates an example procedure for forming a multilayered film including alternately superimposing a layer of substance B on a layer of substance A on the wafer comprising the alternate introduction of gaseous materials A and B into the reaction chamber and the application of light from a xenon flash lamp to the wafer once per introduction of respective gaseous materials A and B into the reaction chamber by which a multilayered film including alternately superimposed layer of substance A on layer of substance B is formed.

According to the procedure shown in Fig. 7, the formation of a multilayered film in which one atomic layer of one substance A is arranged alternately with one atomic layer of another substance B on wafer C as shown in Fig. 8 is possible by controlling the application of light from flash lamp 9 to the sample 7 in association with the introduction of gaseous material into the reaction chamber 1, and by interchanging alternately one gaseous material A with another gaseous material B as shown in Fig. 7, in which designations  $\tau_A$  and  $\tau_B$  designate the pulse intervals when substances A and B are deposited on sample 7, respectively, and  $\tau'_A$  and  $\tau'_B$  designate the times required for material gases of substances A and B to be adsorbed into the surface of sample 7 and C designates the wafer.

Fig. 9 is a graphical representation of a time schedule for the application of pulse waveform light to a monocrystal silicon wafer, the introduction of gaseous material A into the reaction chamber, and the introduction of gaseous material B into the reaction chamber, together with output of pulse waveform light, flow of gaseous material A, flow of gaseous material B, and change of the wafer temperature with time. The graph illustrates an example procedure for forming a film including three alternately superimposed layers of substance A on three layers of substance B on the wafer comprising the alternate introduction of gaseous materials A and B into the reaction chamber and the application of light from a xenon flash lamp to the wafer three times per introduction term of respective gaseous materials A and B into the reaction chamber by which a multilayered film including alternately superimposed layers of substance A on layers of substance B is formed.

According to the procedure shown in Fig. 9, the formation of a multilayered film in which plural atomic layers of one substance A are arranged alternately with plural layers of another substance B at an interval of

some number of layers is possible by controlling the application of light from flash lamp 9 to sample 7, and by interchanging one gaseous material A with another gaseous material B each time as shown in Fig. 10.

Fig. 11 is a graphical representation of a time schedule for the application of pulse waveform light to a monocrystal silicon wafer, the introduction of gaseous material A into the reaction chamber; and the introduction of gaseous material B into the reaction chamber, together with output of the light of pulse waveform, flow of gaseous material A, flow of gaseous material B, and change of the wafer temperature with time. The graph illustrates an example procedure for forming a film including three alternately superimposed layers of substance B on three layers of substance A on the wafer comprising the alternate introduction of gaseous materials A and B into the reaction chamber, the application of light from a xenon flash lamp to the wafer three times per introduction term of respective gaseous materials A and B into the reaction chamber, and changing the wafer temperature in association with the introduction terms of respective gaseous material A and B by which a multilayered film including alternately superimposed layers of substance B on layers of substance A is formed.

According to the procedure shown in Fig. 11, formation of a multilayered film in which plural atomic layers of one substance A are arranged alternately with plural atomic layers of another substance B at an interval of some number of layers is possible by controlling the wafer temperature in association with the introduction of gaseous material into reaction chamber 1 to be entirely adsorbed on the whole surface of sample 7.

In the present invention, it is preferable that the pulse interval is more than the time required for gaseous material to be entirely adsorbed into the whole surface of sample 7. Further, it is preferable that the application of pulse waveform light to sample 7, after the interchange of one gaseous material A with another gaseous material is carried out after the lapse of the time required for another gaseous material B to be entirely adsorbed into the whole surface of the sample.

The above-mentioned examples are examples in which a multilayered structure comprised of different material layers is formed in the same reaction chamber. However, the multilayered structure can be formed by using some number of reaction chambers communicating with each other properly corresponding to substances to be deposited.

Fig. 13 is a graphical representation of a time schedule for the application of pulse waveform light to a monocrystal silicon wafer, the introduction of gaseous material A into the reaction chamber, and the introduction of gaseous material B into the reaction chamber, together with an output of pulse waveform light, flow of gaseous material A, flow of gaseous material B, and change of the wafer temperature with time. The graph illustrates an example procedure for forming a film including three alternately superimposed layers of substance B on three layers of substance A on the wafer comprising forming a layer of substance A according to a conventional vapor deposition method without applying pulse waveform light to the wafer and forming plural layers of substance B on the layer of substance A by applying pulse waveform light to the wafer according to the present invention.

According to the procedure in Fig. 13, a multilayered structure can be formed as shown Fig. 14 in which A designates a film formed by conventional chemical vapor deposition and B designates a film formed by applying light from flash lamp 9 to sample 7 according to the present invention and C designates a wafer. This procedure combines the formation of film by a conventional vapor deposition with the above-mentioned method.

Further in the procedure shown in Fig. 13, it is apparent that it is possible to combine the device for forming a film without using a flash lamp with the reaction chamber using the flash lamp.

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## Claims

1. A vapor depositing method comprising placing a sample in a reaction chamber, and exposing the sample to gaseous material introduced into the reaction chamber from a gas source, applying pulse

waveform light to the sample from a source of pulse waveform light, whereby a film formed of an atomic layer or of plural atomic layers is produced with every application of pulse waveform light to the sample.

2. A vapor depositing method as claimed in claim 1 wherein the application of pulse waveform light to the sample is controlled in association with the introduction of gaseous material into the reaction chamber and a plurality of gaseous materials are interchanged at the same time or alternately in the reaction chamber whereby a film comprised of mixed crystals or different materials forms an atomic layer or plural atomic layers.

3. A vapor depositing method as claimed in claim 2 wherein a pulse waveform light is applied one or more times while introducing gaseous materials into the reaction chamber.

4. A vapor depositing method as claimed in claim 1 further comprising the steps of separating the adsorbed substance from the surface of the sample by heating the sample before applying pulse waveform light, lowering the temperature of the sample to a temperature lower than a separation temperature of the adsorbed substance from the sample, and exposing the sample to gaseous material introduced into the reaction chamber.

5. A vapor depositing method as claimed in claim 1 further comprising the steps of heating the sample at a constant temperature before or after forming a film by application of pulse waveform light or during application of pulse waveform light to the sample whereby gaseous material reacts chemically to form the film.

6. A vapor depositing method as claimed in claim 1 wherein said pulse waveform light is light from a flash lamp.

7. A vapor depositing apparatus comprising a reaction chamber in which a sample is put, a gas source from which gaseous material is introduced into the reaction chamber, and a source of pulse waveform light from which pulse waveform light is applied to the surface of the sample through a transparent window of the reaction chamber.

8. A vapor depositing apparatus as claimed in claim 7 further comprising a control system for controlling the application of pulse waveform light to the sample from the source of pulse waveform light in association with the introduction of gaseous material into the reaction chamber.

9. A vapor depositing apparatus as claimed in claim 7 further comprising a heater for heating the sample.

10. A vapor depositing apparatus as claimed in claim 9 wherein the heater is a high frequency heater.

11. A vapor depositing apparatus as claimed in any of claims 7 wherein the source of pulse waveform light is from a flash lamp.

12. A vapor depositing method as claimed in claim 2 further comprising the steps of separating the adsorbed substance from the surface of the sample by heating the sample before applying pulse waveform light, lowering the temperature of the sample to a temperature lower than a separation temperature of the adsorbed substance from the sample, and exposing the sample to gaseous material introduced into the reaction chamber.

13. A vapor depositing apparatus as claimed in claim 8 further comprising a heater for heating the sample.

14. A vapor depositing apparatus as claimed in any of claims 8 wherein the source of pulse waveform light is from a flash lamp.

15. A vapor depositing apparatus as claimed in any of claims 9 wherein the source of pulse waveform light is from a flash lamp.

16. A vapor depositing apparatus as claimed in any of claims 10 wherein the source of pulse waveform light is from a flash lamp.

17. A vapor deposition method comprising; placing a sample in a reaction chamber; supplying at least one



gaseous material to said reaction chamber; exposing said sample to said gaseous material; applying pulse waveform light to said sample for a predetermined period of time; whereby an atomic layer of said at least one gaseous material is produced with each application of pulse waveform light.

18. The vapor deposition method according to claim 17 including; controlling the application of pulse waveform light to coincide with the introductions of said at least one gaseous material; whereby single or multiple atomic layers of said at least one gaseous material are produced with each application of pulse waveform light.

19. The vapor deposition method according to claim 18 wherein said at least one gaseous material is a plurality of different gaseous materials selectively interchanged; whereby a plurality of atomic layers is selectively alternately produced with each application of pulse waveform light.

20. The vapor deposition method according to claim 19 wherein said pulse waveform light is selectively applied a plurality of times during the introduction of a selected at least one gaseous material.

21. The vapor deposition method according to claim 18 including; heating the sample to separate the absorbed substance from the surface of the sample; lowering the temperature of the sample below the separation temperature of the absorbed substance; and exposing the sample to gaseous material introduced into said reaction chamber.

22. The vapor deposition method according to claim 18 including; heating said sample to a constant temperature for a preselected time whereby gaseous material reacts chemically to form a film.

23. A vapor deposition apparatus comprising; a reaction chamber; said reaction chamber having a window; a source for supplying at least one gaseous material to said reaction chamber; pulse waveform light source means for applying pulse waveform light to a sample placed in said chamber; said pulse waveform light being applied through said window.

24. The vapor deposition apparatus according to claim 23 including; control means for selectively controlling the application of pulse waveform light to said sample according to the introduction of said at least one gaseous material into said reaction chamber.

25. The vapor deposition apparatus according to claim 24 including heating means for heating said sample.

26. The vapor deposition apparatus according to claim 25 in which said heating means comprises a high frequency oscillator heater.

27. The vapor deposition apparatus according to claim 24 in which said pulse waveform light source is a flash lamp.

28. The vapor deposition method according to claim 18 in which said pulse waveform light source is a flash lamp.

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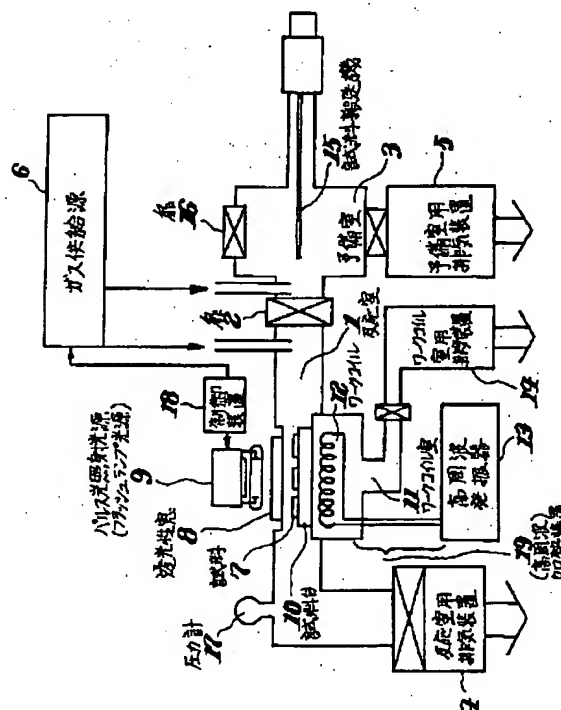
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審査請求 未請求 請求項の数11(全 17 頁)

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最終頁に続く

〔構成〕 反応室 1 内に設置された試料 7 をガス供給源 6 より導入された原料ガスに曝した状態で、パルス光照射光源 9 によりパルス光を試料 7 に照射することによって 1 回の照射毎に 1 原子層又は数原子層の薄膜を成長させる。



## 【特許請求の範囲】

【請求項1】 反応室(1)内に設置された試料(7)をガス供給源(6)より導入された原料ガスに曝した状態で、パルス光照射光源(9)によりパルス光を試料(7)に照射することによって1回の照射毎に1原子層又は数原子層の薄膜を成長させることを特徴とする気相成長方法。

【請求項2】 反応室(1)内への原料ガスの導入とパルス光の照射を制御装置(18)により関連付けて制御し、2種以上の原料ガスを同時に又は交互に入れ換え、試料(7)に混晶物質や異種物質を原子層状に成長させることを特徴とする請求項1の気相成長方法。

【請求項3】 原料ガスの導入中にパルス光を1回又は2回以上照射することを特徴とする請求項2の気相成長方法。

【請求項4】 パルス光を照射する前に、試料(7)を加熱装置(19)により加熱することにより、試料(7)表面の吸着物を昇温脱離させる工程と、その後試料(7)温度を脱離温度より低くした後、原料ガスを導入して試料(7)を原料ガスに曝す工程とを含むことを特徴とする請求項1~3の気相成長方法。

【請求項5】 パルス光照射による薄膜の形成の前又は後或いはパルス光照射の間に、試料(7)を一定に加熱し、原料ガスを化学的に反応させて薄膜を形成させる工程を含むことを特徴とする請求項1~4の気相成長方法。

【請求項6】 パルス光はフラッシュランプ光であることを特徴とする請求項1~5の気相成長方法。

【請求項7】 試料(7)を設けた反応室(1)と、この反応室(1)内に原料ガスを導入するガス供給源(6)と、反応室(1)内の試料(7)表面に透光性窓(8)を通してパルス光を照射するパルス光照射光源(9)とよりなる気相成長装置。

【請求項8】 ガス供給源(6)による反応室(1)内への原料ガスの導入とパルス光照射光源(9)による試料(7)へのパルス光の照射を関連付けて制御する制御装置(18)を設けることを特徴とする請求項7の気相成長装置。

【請求項9】 試料(7)を加熱する加熱装置(19)を具備してなる請求項7、8の気相成長装置。

【請求項10】 加熱装置(19)は高周波加熱装置であることを特徴とする請求項9の気相成長装置。

【請求項11】 パルス光照射光源(9)はフラッシュランプ光源であることを特徴とする請求項7~10の気相成長装置。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は反応室内の試料に原料ガスの供給により原子層状に薄膜を気相成長する方法及び装置に関する。

## 【0002】

【従来の技術】 通常の気相成長方法は図1を参照して説明すると、反応室1内にガス供給源6により原料ガスを流通させながら反応室1内の試料7を高周波加熱装置19により加熱して試料7表面にCVD膜を成長させる方法であり、このような方法では試料7表面に吸着と反応が連続的に生じ、原子層状の薄膜形成は極めて困難であった。

【0003】 従来、原子層状に成長させる気相成長では、対象物質として化合物半導体が用いられていた。例えばGaAsにおいて、Asの上にはAsが付着しないという特徴を生かして原子層状にGaAsを形成する方法がある。

【0004】 又、原料ガスを表面に吸着させ、その後気相中の原料ガスを排気し、光照射などの方法で吸着した物質を分解・反応させるということを繰り返す方法がある。

## 【0005】

【発明が解決しようとする課題】 しかしながら、前者の方法ではSiやGeなどの元素半導体で実現されていない。後者の方法では、有機系あるいはハロゲン系の原料ガスで実現されうるが、水素化物系では、気相中の原料ガス排気時に、表面から吸着物質が脱離するという課題があった。

【0006】 本発明は原料ガスが試料に単分子吸着し、しかもその吸着物が分解・反応後、次の吸着が完了するまでに時間を要するという現象を利用するもので、原料ガスの試料表面への吸着と表面での吸着した原料ガスの分解・反応を分離するために、試料表面に原料ガスを吸着させた後、パルス光により、吸着物を瞬時に分解・反応させることを特徴とし、その目的は原子層状に形成することにある。

## 【0007】

【課題を解決するための手段】 本発明方法は上記の課題を解決し上記の目的を達成するため、図1に示すように反応室1内に設置された試料7をガス供給源6より導入された原料ガスに曝した状態で、パルス光照射光源9によりパルス光を試料7に照射することによって1回の照射毎に1原子層又は数原子層の薄膜を成長させることを特徴とする。

【0008】 又、本発明装置は同じ課題を解決し同じ目的を達成するため、図1に示すように試料7を設けた反応室1と、この反応室1内に原料ガスを導入するガス供給源6と、反応室1内の試料7表面に透光性窓8を通してパルス光を照射するパルス光照射光源9とよりなる。

## 【0009】

【作用】 このような構成であるから、反応室1内にガス供給源6より原料ガスを導入して反応室1内の試料7をこの原料ガスで曝した状態で、パルス光照射光源9によりパルス光を試料7に照射することによって1回の照射

毎に1原子層又は数原子層の薄膜を成長させることができることになる。

【0010】換言すれば、試料7表面に原料ガスを吸着させた後、パルス光により吸着物を瞬時に分解・反応させ、原子層状に薄膜を形成することができることになる。

【0011】

【実施例】図1は本発明方法及び装置の1実施例の概略構成説明図である。本実施例は、反応室1、この反応室1に扉2を介して連なる予備室3、反応室1及び予備室3をそれぞれ減圧するための反応室、予備室用排気装置4、5、反応室1及び予備室3にガスを供給するためのガス供給源6及び反応室1内の試料7の表面に透光性窓8を通してフラッシュランプ光を照射するためのフラッシュランプ光源9とを備えている。

【0012】そして試料7を補助加熱するための試料台10とワークコイル室11、高周波をワークコイル室11内のワークコイル12に供給するための高周波発振器13、ワークコイル室11を減圧するためのワークコイル室用排気装置14、反応室1に試料7を搬送するために予備室3内に設けられた試料搬送機15、外部から試料7を予備室3に搬入するために予備室3に設けられた扉16及びガス供給源6による反応室1内への原料ガスの導入とフラッシュランプ光源9による試料7へのフラッシュ光の照射を関連付けて制御する制御装置18とを備えた構成となっている。なお、17は圧力計である。

【0013】次に、上述した装置を用いて膜を形成する方法について説明する。膜の形成は、次のような手順で行う。①反応室1とワークコイル室11をそれぞれ排気装置4、14で真空排気する。②次に真空排気状態の反応室1内にガス供給源6より水素などのキャリアガスを流入させる。

【0014】③予備室3を窒素などのガスで大気圧状態にし扉16を開け、試料7を予備室3内の試料搬送機15に乗せた後、扉16を締める。④反応室1内に流入させているガスと同種のガスを予備室3内に流入させながら、予備室3内を排気装置5で減圧にする。

【0015】⑤扉2を開け、試料7を試料搬送機15により予備室3内から反応室1内に搬送し、試料台10上に乗せ、搬送機15を予備室3内に戻し、扉2を閉める。⑥ワークコイル12に高周波発振器13より高周波を加え、試料台10を加熱し、その熱で試料7を加熱する。

【0016】なお、この加熱はフラッシュランプ光の照射時の原料ガスの分解・反応を促進させるため、もしくは、試料7表面の不要吸着物を昇温脱離させるため、もしくは、通常の化学気相成長法で薄膜を形成するために用いる。

【0017】⑦その後、原料ガスをガス供給源6より反応室1に流入させる。⑧次に、原料ガスが試料7表面に

吸着するのに必要な時間の後、フラッシュランプ光をフラッシュランプ光源9より透光性窓8を通して試料7表面に照射する。

【0018】ここで、反応室1内への原料ガスの流入とフラッシュランプ光の照射を制御装置18により関連付けて制御し、2種以上の原料ガスを同時にもしくは交互に入れ替えてもよい。またフラッシュランプ光を照射後、別の原料ガスを流入させ、試料7の加熱により、異種の物質を成長させてもよい。

【0019】このような工程でたとえば単結晶シリコン上にゲルマニウムを形成する場合の手順の一例について図2を用いて説明する。反応室1に水素ガス200cc/minを流入させ、反応室1内圧力270Paとなっている状態で、単結晶シリコンウェハ(試料7)を試料台10に乗せ、図2の時間 $t_1$ で単結晶シリコンウェハを加熱(ウェハ温度 $T_c$ )し、400℃以上の温度 $T_0$ のウェハ表面の不要吸着物を昇温脱離させたのち、図2の時間 $t_2$ で230~290℃の温度 $T_c$ に下げる。

【0020】次に、時間 $t_3$ でゲルマンガス( $GeH_4$ )を反応室1内で1~20Paの分圧になるように導入し、ゲルマンガスが試料表面に吸着するのに要する時間 $\tau_c$ 以上経た後の時間 $t_4$ よりパルス幅約1msec、パルス強度20J/cm<sup>2</sup>のキセノンフラッシュランプ光を単結晶シリコンウェハ表面に繰り返し照射した( $\tau_c$ はパルス光の繰り返し間隔)。

【0021】このような方法でゲルマニウムを堆積させた時の1パルス当たりの堆積ゲルマニウムの膜厚を調べた。全圧力( $GeH_4 + H_2$ )が280Pa、ゲルマンガス( $GeH_4$ )分圧が13Paでパルス間隔 $\tau_c = 2.0$ 秒間の場合、図3に示すように、260~275℃の範囲で、温度によらず、ウェハの面方位がSi(100)とSi(111)上でそれぞれ1原子層/パルスのゲルマニウムの堆積が認められる。

【0022】図3中、○はSi(111)上での1パルス当たりの堆積ゲルマニウムの厚さ、●はSi(100)上での1パルス当たりの堆積ゲルマニウムの厚さ、aの破線はGe(111)の1原子層の厚さ、bの破線はGe(100)の1原子層の厚さを示す(以下図4~5同じ)。

【0023】パルス間隔が2.0秒間、全圧力( $GeH_4 + H_2$ )が280Pa、ウェハ補助加熱温度268℃の場合、ゲルマンガス分圧が13Pa以上で、図4に示すように1原子層/パルスのゲルマニウムの堆積が認められる。

【0024】全圧力( $GeH_4 + H_2$ )が280Pa、ウェハ補助加熱温度が268℃の場合、ゲルマンガス分圧が4.5Paでも、図5に示すように、パルス間隔が長くなれば、1原子層/パルスのゲルマニウムの堆積が認められる。

【0025】なお、230~290℃の温度では、フラ

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ッシュランブ光を照射しなければ、ゲルマニウムの堆積は認められない。ウェハの面方位を変えると、ウェハ補助加熱温度が268℃、パルス間隔が20秒間、全圧力( $\text{GeH}_4 + \text{H}_2$ )が280Pa、ゲルマンガス分圧が13Paの場合、図6に示すように、それぞれの面方位に対して、1原子層/パルスのゲルマニウムの堆積が認められる。

【0026】以上述べたように、試料を原料ガスに曝した状態で、パルス光を照射することにより、1回の照射ごとに、1原子層の薄膜を成長させることができることは明らかである。また、2種以上の原料ガスを同時に流入させ、混晶物質を原子層状に成長させることができることは、容易に類推できる。

【0027】さらに、反応室内への原料ガスの導入とフラッシュランブ光の照射を制御装置18により関連付けて制御し、①2種以上の原料ガスを図7に示すように交互に入れ換え、図8に示すような1原子層ごとに異種の物質のある多層原子層状の薄膜を形成することができる。ここで、 $\tau_A$ 、 $\tau_B$ はそれぞれA、B物質を形成するときのパルス間隔、 $\tau'_A$ 、 $\tau'_B$ はそれぞれA、B物質の原料となるガスが試料表面に吸着するのに要する時間、Cはウェハである。

【0028】②2種以上の原料ガスを図9に示すようにある時間毎に入れ換え、図10に示すような数原子層あるいは数十原子層ごとに異種の物質のある多層膜を形成することができる。

【0029】また③反応室内への原料ガスの導入とウェハの補助加熱温度も図11のように関連付けて制御し、図12に示すような数原子層あるいは数十原子層ごとに異種の物質のある多層膜を形成することができることは明らかである。

【0030】なお、上記において、パルス間隔は原料ガスが試料表面に完全に吸着被覆するのに要する時間以上であることが望ましく、また異種の原料ガスに入れ換えた後のパルス光の照射は、入れ換えた後の異種の原料ガスが試料表面に完全に吸着被覆するのに要する時間の後に行うことが望ましい。

【0031】また上記方法は、同一の反応室で異種の物質の多層構造を実現する例であるが、同様の反応室をつなげて、物質毎に、反応室を使い分け、異種物質の多層構造を実現してもよい。

【0032】また、パルス光照射光源9を用いない別の手段、例えば、図13に示すように、通常の気相成長方法による薄膜形成と上記方法とを組合せ、図14に示すような多層構造も実現可能になることは明らかである。図14でAは通常の化学気相成長方法を用いて形成した薄膜、Bはフラッシュランブ光により形成した薄膜、Cはウェハを示す。

【0033】なお、図13では、同一の反応室内で図14に示すような多層構造を実現する手順を示したが、フ

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ラッシュランブを用いない別の手段での薄膜形成する機能をフラッシュランブを用いて薄膜形成する反応室につなげて、図14に示すような多層構造を実現できることは明らかである。

【0034】

【発明の効果】上述の説明より明らかなように本発明によれば、試料7を設けた反応室1と、この反応室1内に原料ガスを導入するガス供給源6と、反応室1内の試料7表面に透光性窓8を通してパルス光を照射するパルス光照射光源9とよりなるので、反応室1内にガス供給源6より原料ガスを導入して反応室1内の試料7をこの原料ガスで曝した状態で、パルス光照射光源9によりパルス光を試料7に照射することによって1回の照射毎に1原子層又は数原子層の薄膜を成長させることができる。

【図面の簡単な説明】

【図1】本発明方法及び装置の1実施例の概略構成説明図である。

【図2】キセノンフラッシュランブ光を単結晶シリコンウェハ表面に繰り返し照射した時のゲルマニウムを堆積させる手順の1例を示す説明図である。

【図3】キセノンフラッシュランブ光を単結晶シリコンウェハ表面に繰り返し照射した時の、1パルス当たりの堆積ゲルマニウムの膜厚の単結晶シリコンウェハの温度依存性の説明図である。

【図4】キセノンフラッシュランブ光を単結晶シリコンウェハ表面に繰り返し照射した時の、1パルス当たりの堆積ゲルマニウムの膜厚の反応室内のゲルマンガス分圧依存性の説明図である。

【図5】キセノンフラッシュランブ光を単結晶シリコンウェハ表面に繰り返し照射した時の、1パルス当たりの堆積ゲルマニウムの膜厚のパルス間隔依存性の説明図である。

【図6】キセノンフラッシュランブ光を単結晶シリコンウェハ表面に繰り返し照射した時の、1パルス当たりの堆積ゲルマニウムの膜厚の基板面方位依存性の説明図である。

【図7】反応室内への原料ガスの導入とフラッシュランブ光の照射を関連付けて制御し、A物質の原料となるガスとB物質の原料となるガスを交互に入れ換え、1原子層ごとに異種の物質のある多層原子層状の薄膜を形成する手順の1例を示す説明図である。

【図8】図7に示す手順で1原子層ごとにAとBの物質のある多層原子層状の薄膜を形成した試料の断面図である。

【図9】反応室内への原料ガスの導入とフラッシュランブ光の照射を関連付けて制御し、A物質の原料となるガスとB物質の原料となるガスのある時間毎に入れ換え、数原子層あるいは数十原子層ごとに異種の物質のある多層膜を形成する手順の1例を示す説明図である。

【図10】図9に示す手順で数原子層あるいは数十原子

層ごとに異種の物質のある多層膜を形成した試料の断面図である。

【図11】反応室内への原料ガスの導入とフラッシュランプ光の照射を関連付けて制御し、かつ反応室内への原料ガスの導入と基板の補助加熱温度も関連付けて制御し、数原子層あるいは数十原子層ごとに異種の物質のある多層膜を形成する手順の1例を示す説明図である。

【図12】図11に示す手順で数原子層あるいは数十原子層ごとに異種の物質のある多層膜を形成した試料の断面図である。

【図13】通常の気相成長方法による薄膜形成とフラッシュランプ光を用いた薄膜形成を組合せ、異種物質の多層構造も実現する手順の1例を示す説明図である。

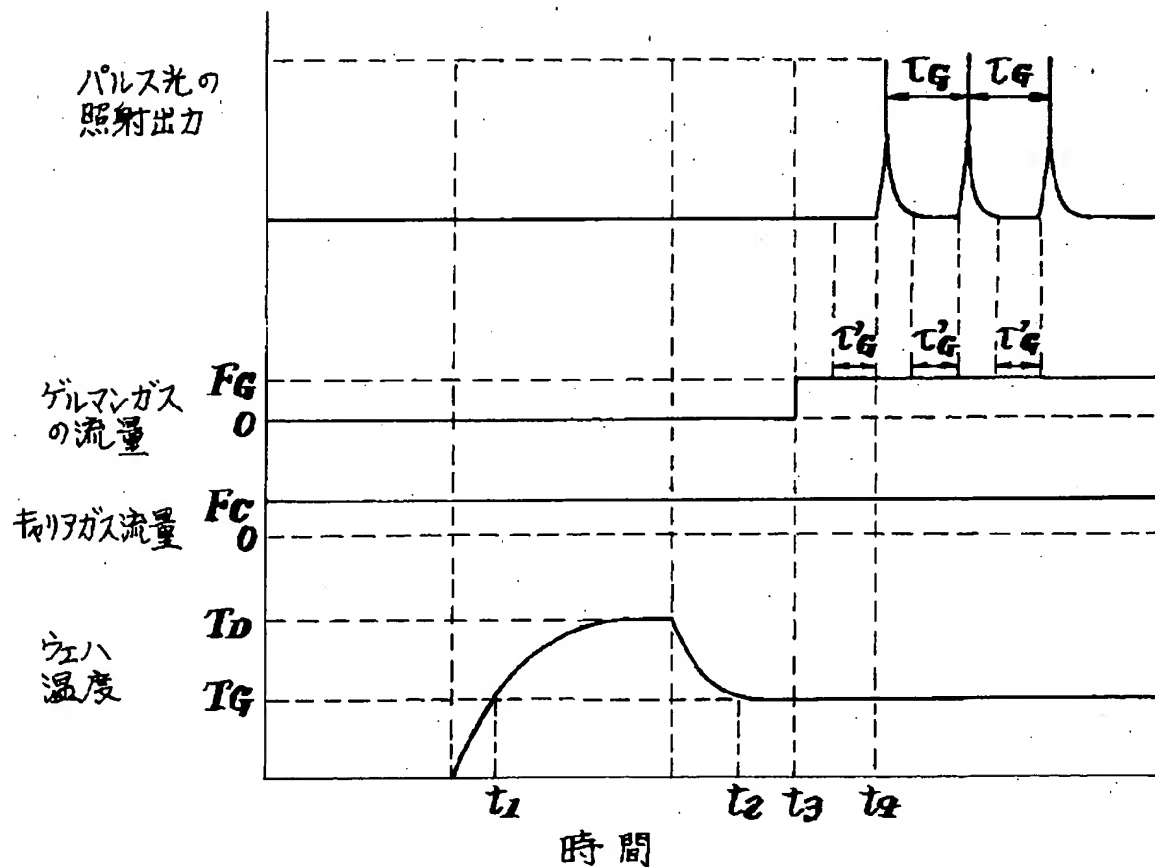
【図14】図13に示す手順で異種物質の多層構造も実現した試料の断面図である。

【符号の説明】

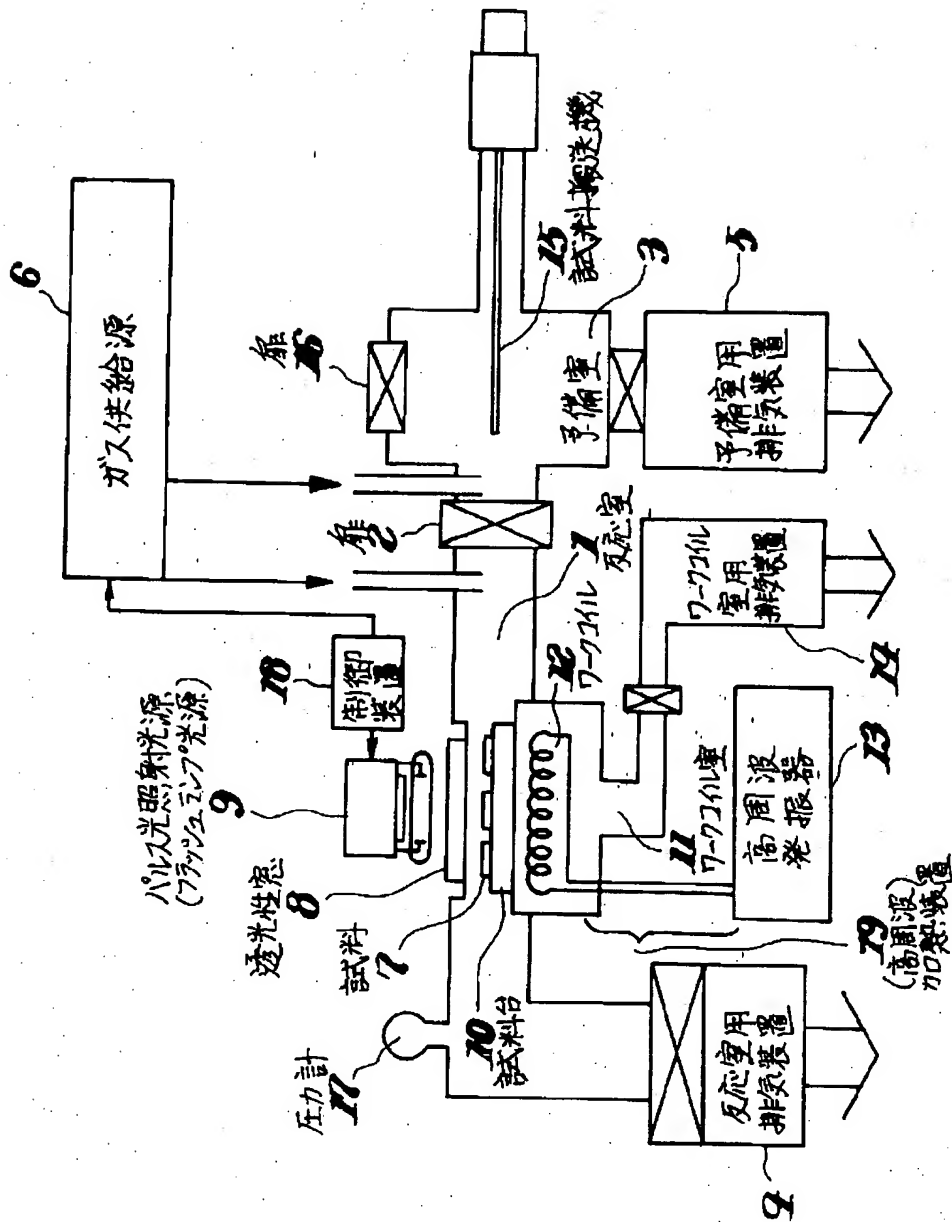
- 1 反応室  
2 扉

- 3 予備室  
4 反応室用排気装置  
5 予備室用排気装置  
6 ガス供給源  
7 試料  
8 透光性窓  
9 パルス光照射光源（フラッシュランプ光源）  
10 試料台  
11 ワークコイル室  
12 ワークコイル  
13 高周波発振器  
14 ワークコイル室用排気装置  
15 試料搬送機  
16 扉  
17 圧力計  
18 制御装置  
19 （高周波）加熱装置

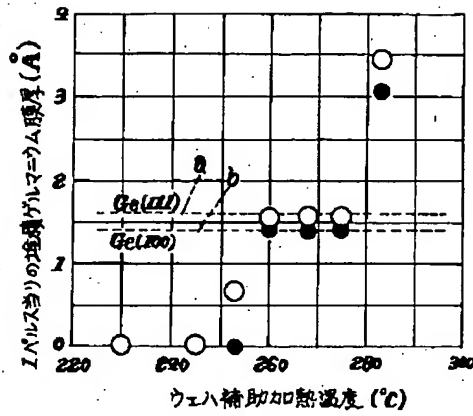
【図2】



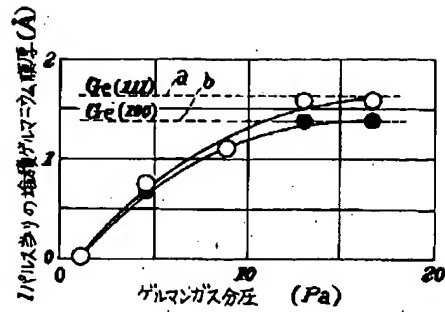
【図1】



【図3】



【図4】



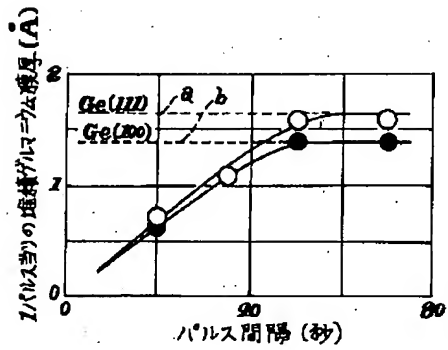
【図8】

B
A
B
A
C

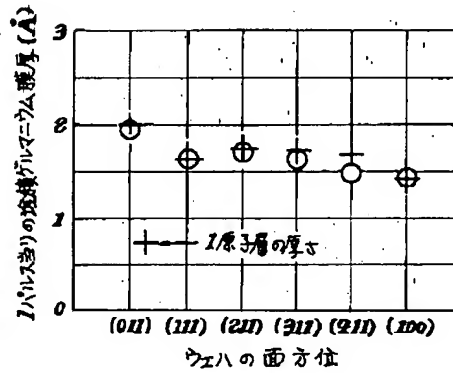
【図10】

B
B
B
A
A
A
C

【図5】



【図6】



【図12】

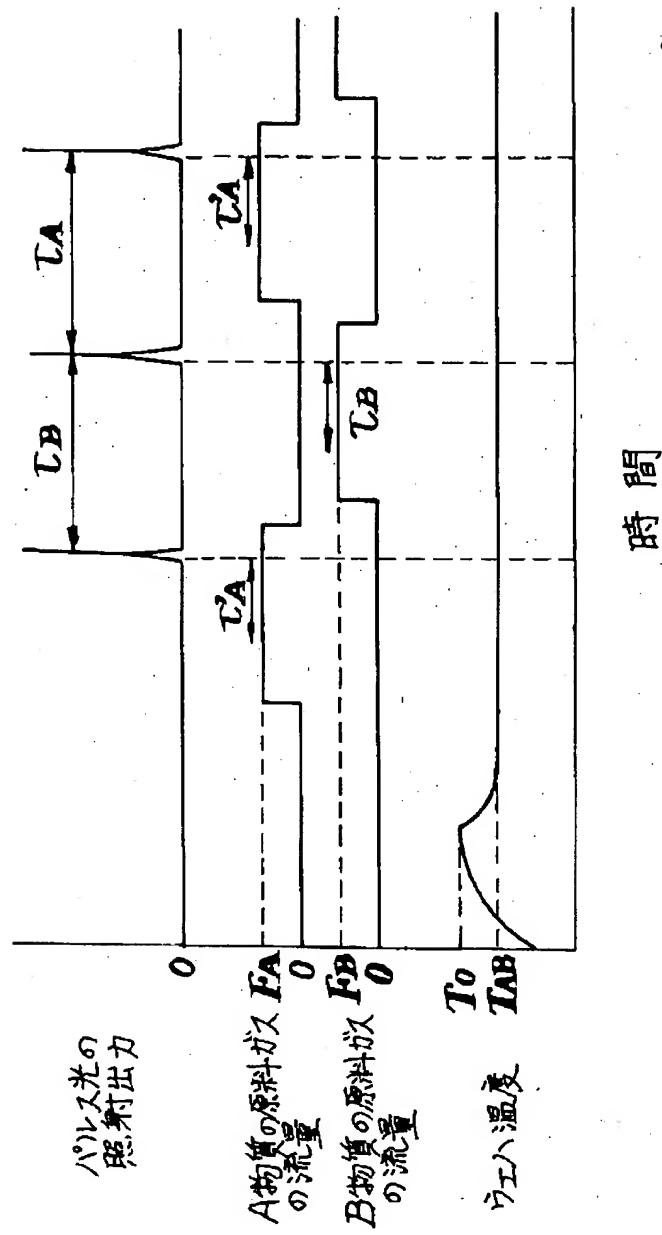
A
B
B
B
A
A
A
C

【図14】

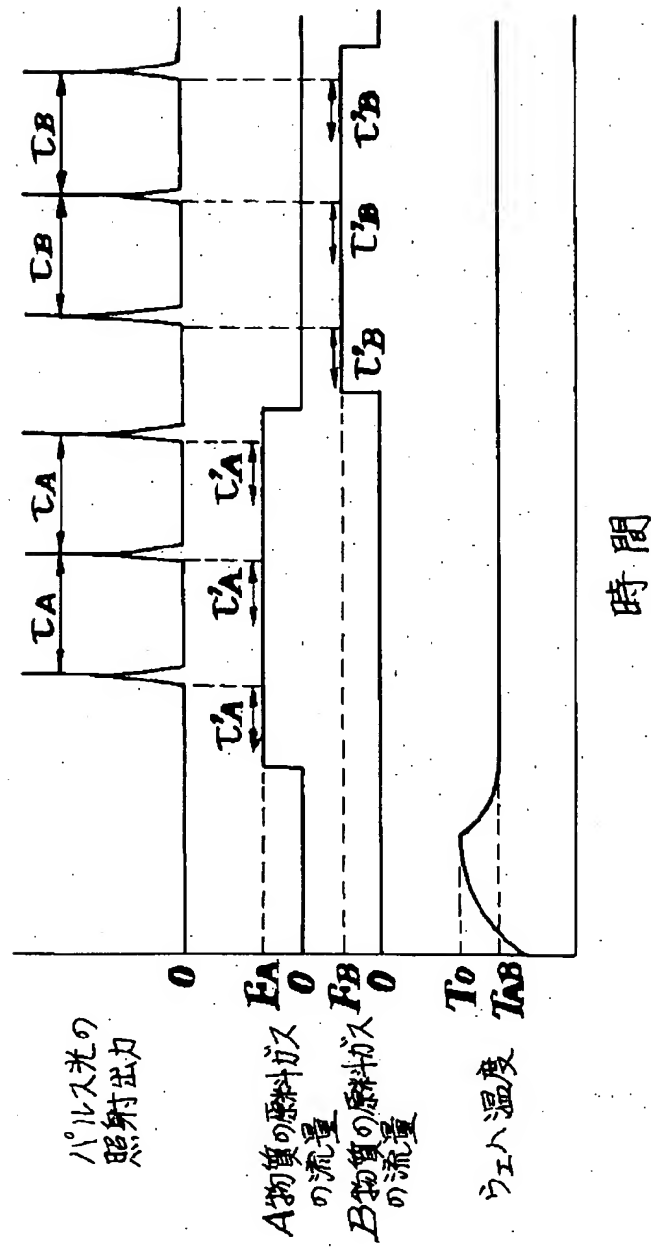
A
B
B
B
A
C



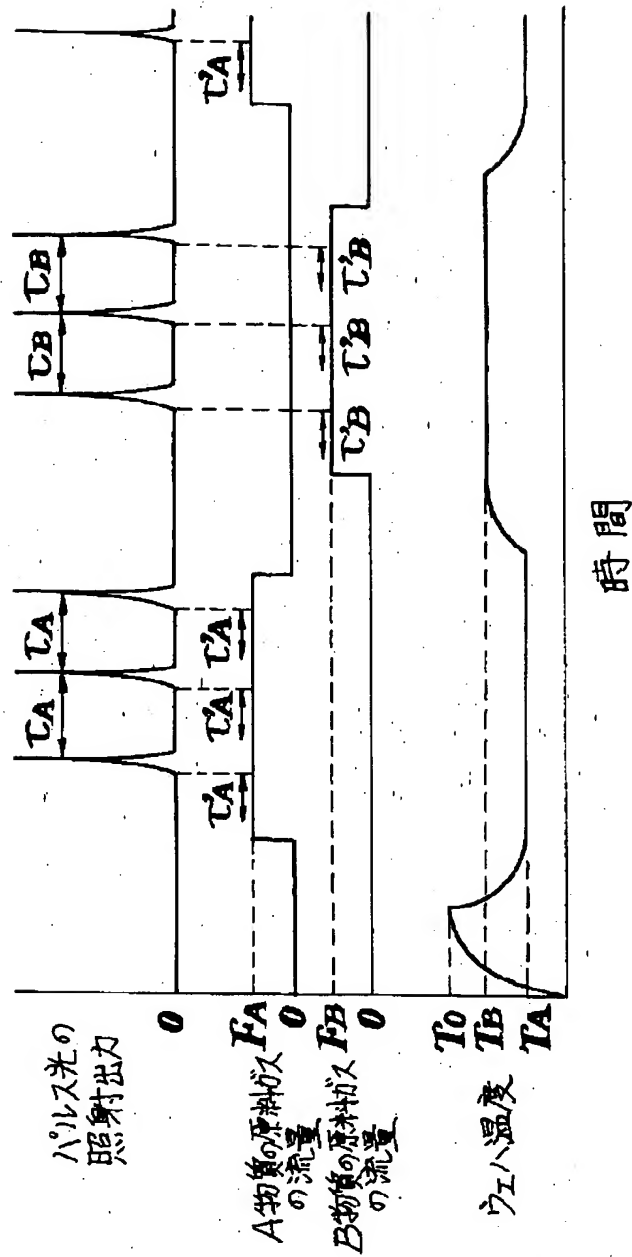
【図7】



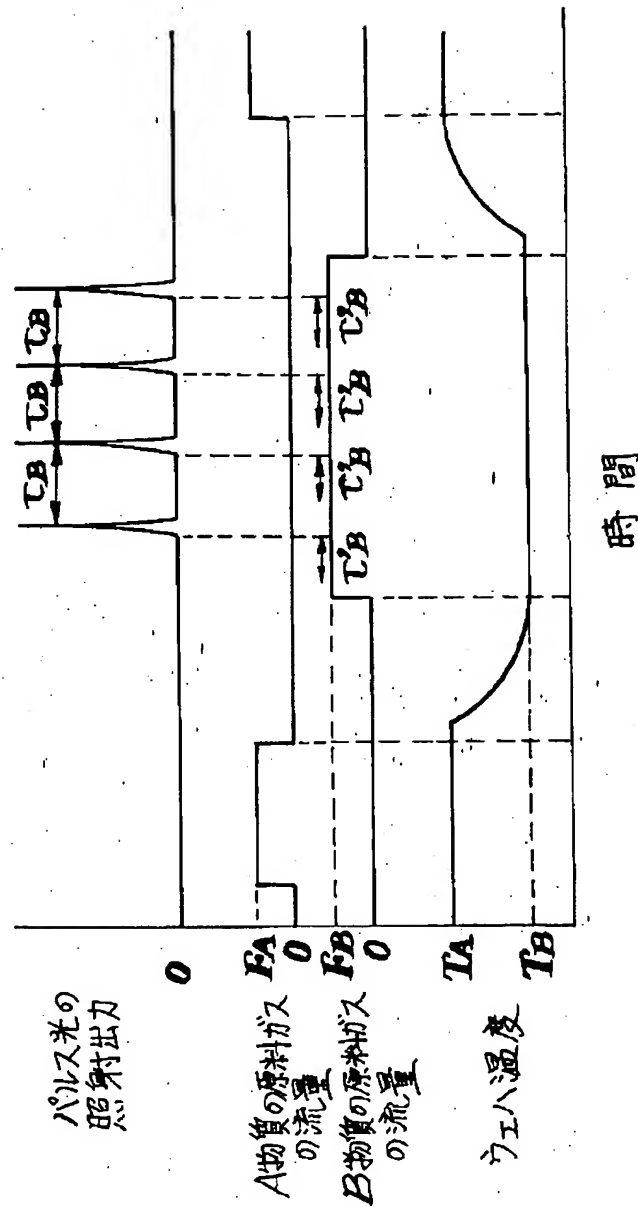
【図9】



【図11】



【図13】



【手続補正書】

【提出日】平成3年6月26日

【手続補正1】

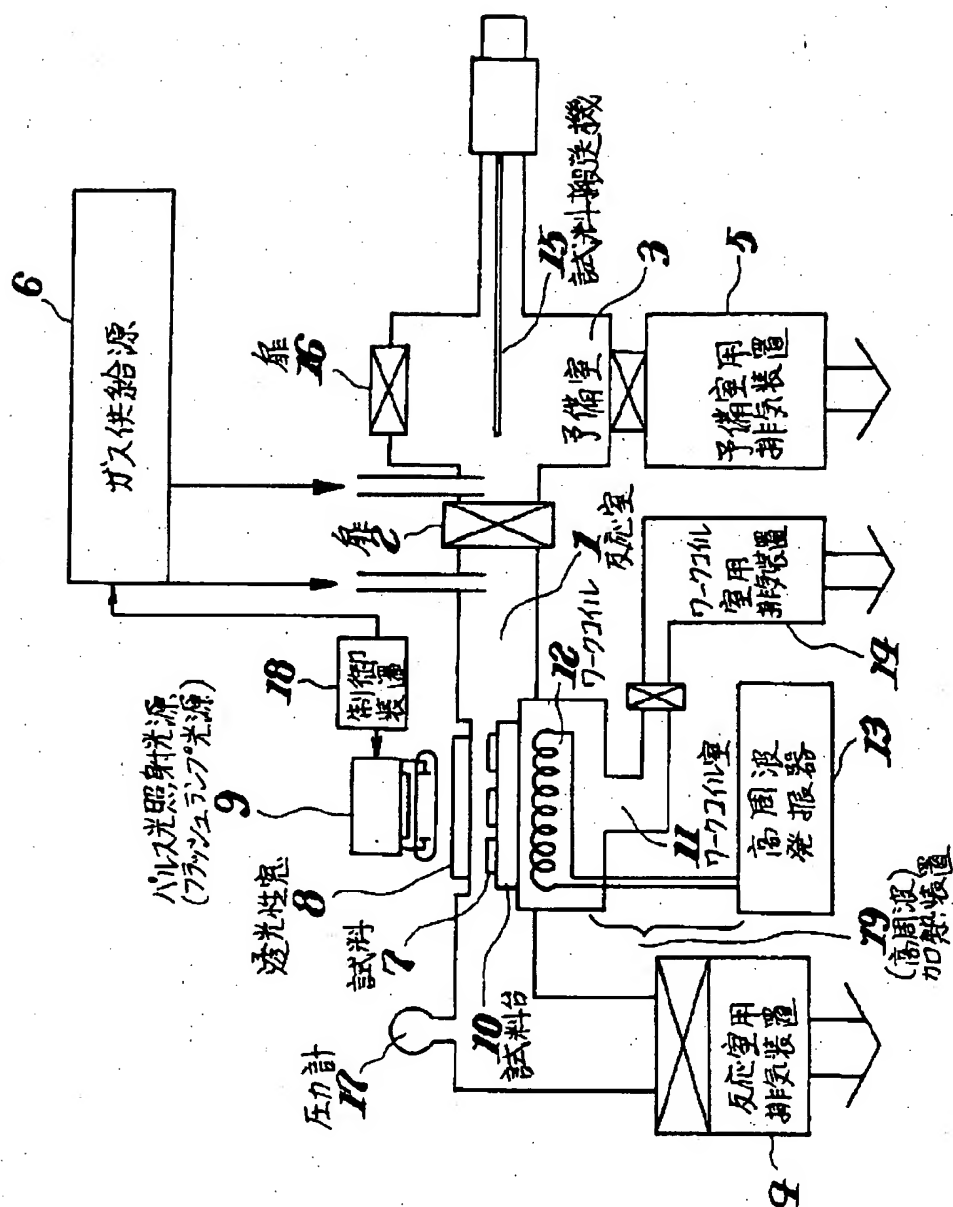
【補正対象書類名】図面

【補正対象項目名】全図

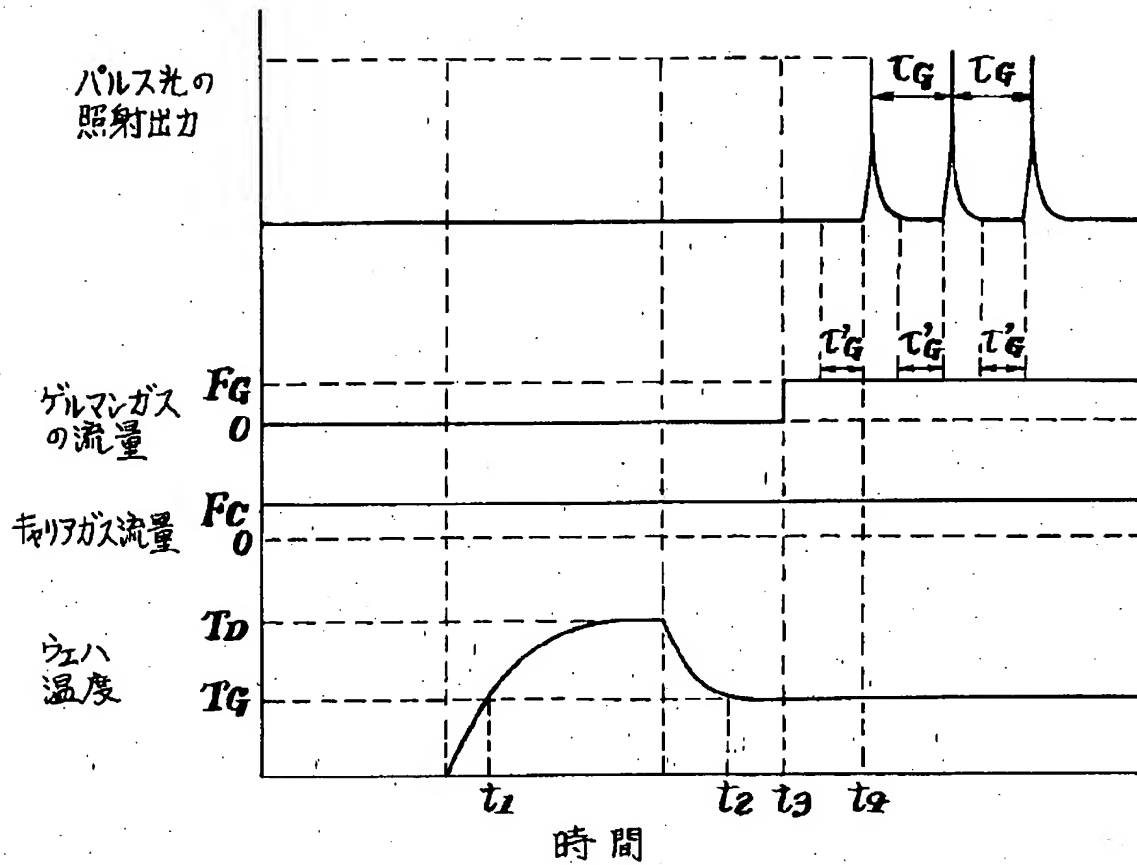
【補正方法】変更

【補正内容】

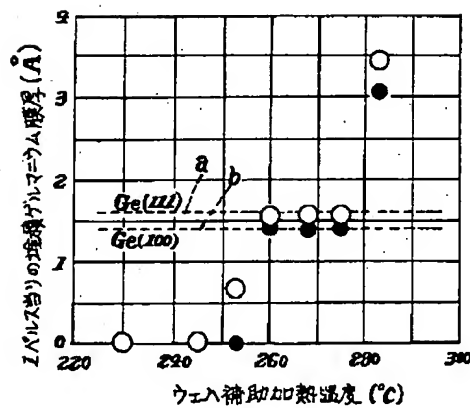
【図1】



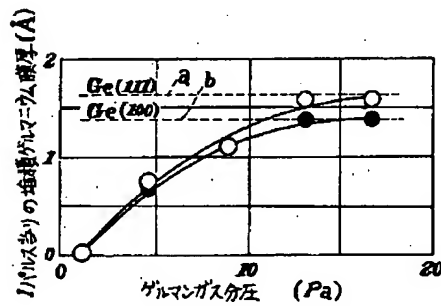
【図2】



【図3】



【図4】



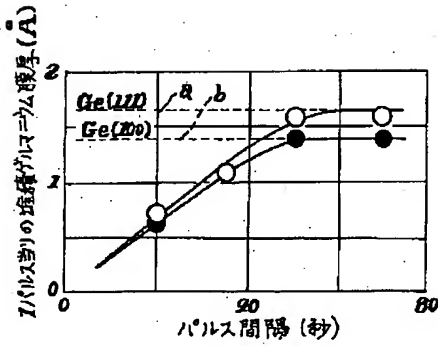
【図8】

B
A
B
A
C

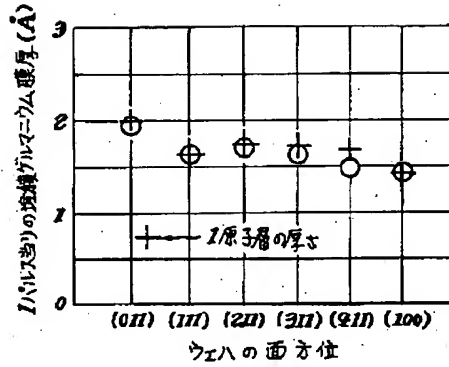
【図12】

A
B
B
B
A
A
A
C

【図5】



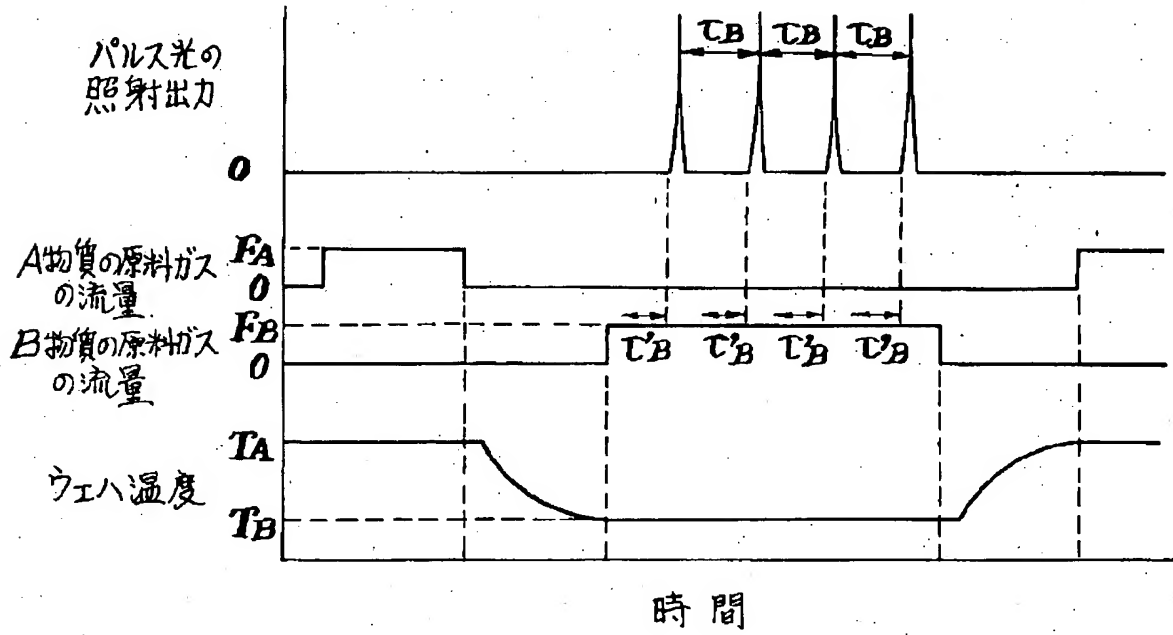
【図6】



【図10】

B
B
B
A
A
A
C

【図13】

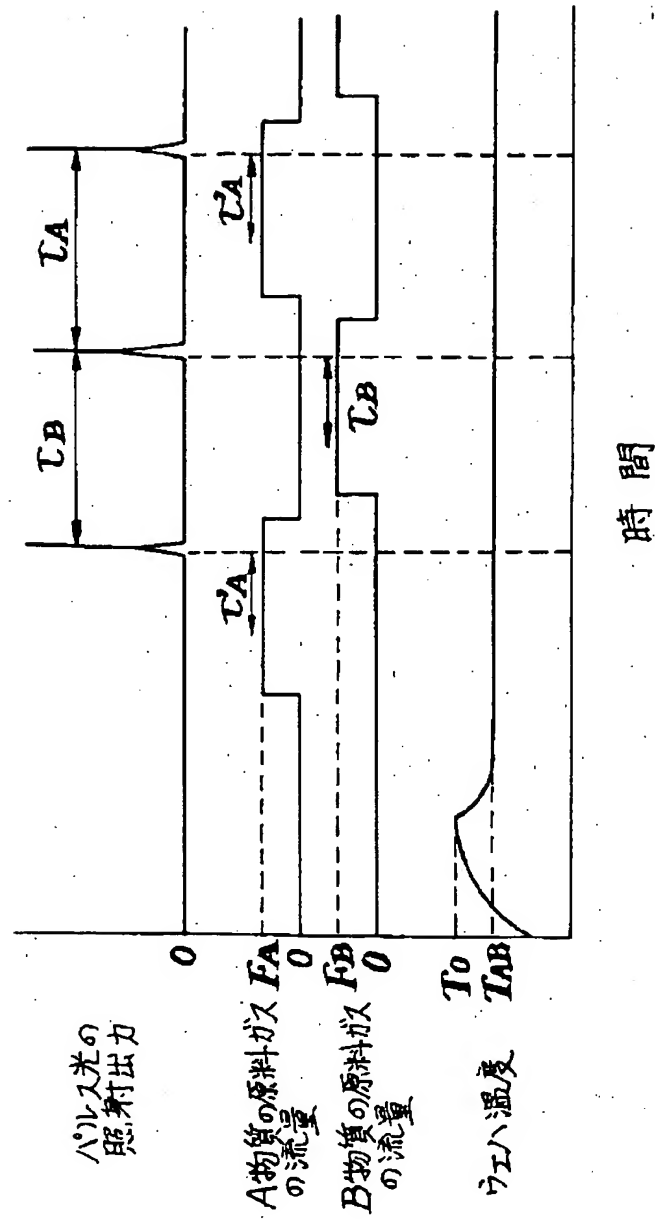


【図14】

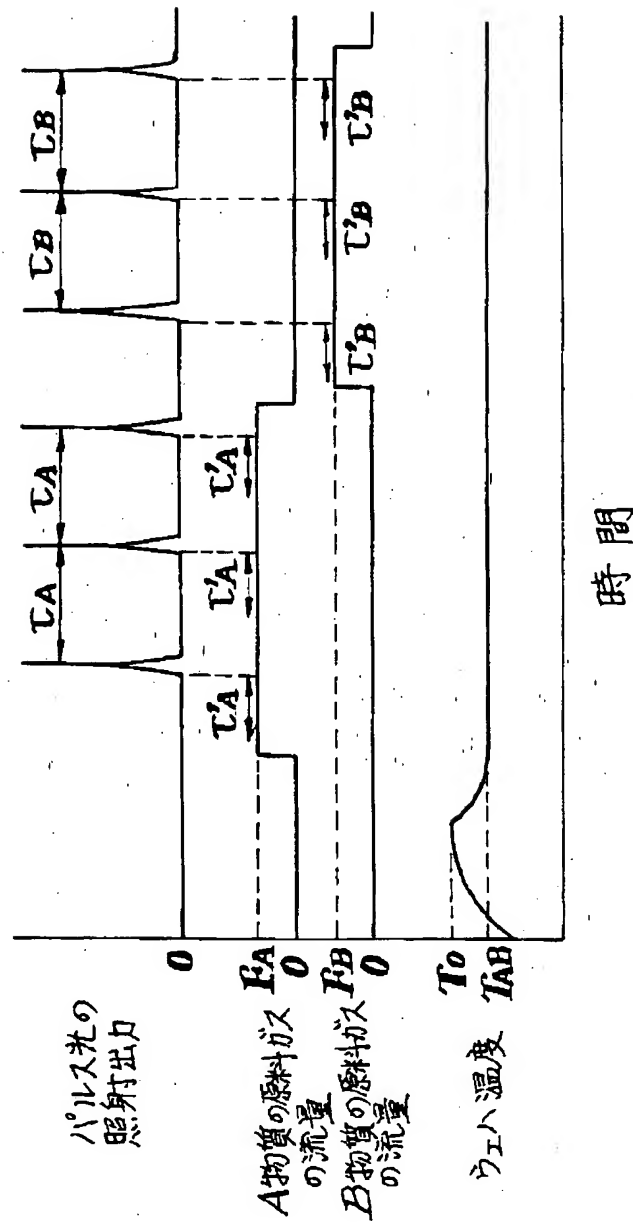
A
B
B
B
B
A
C



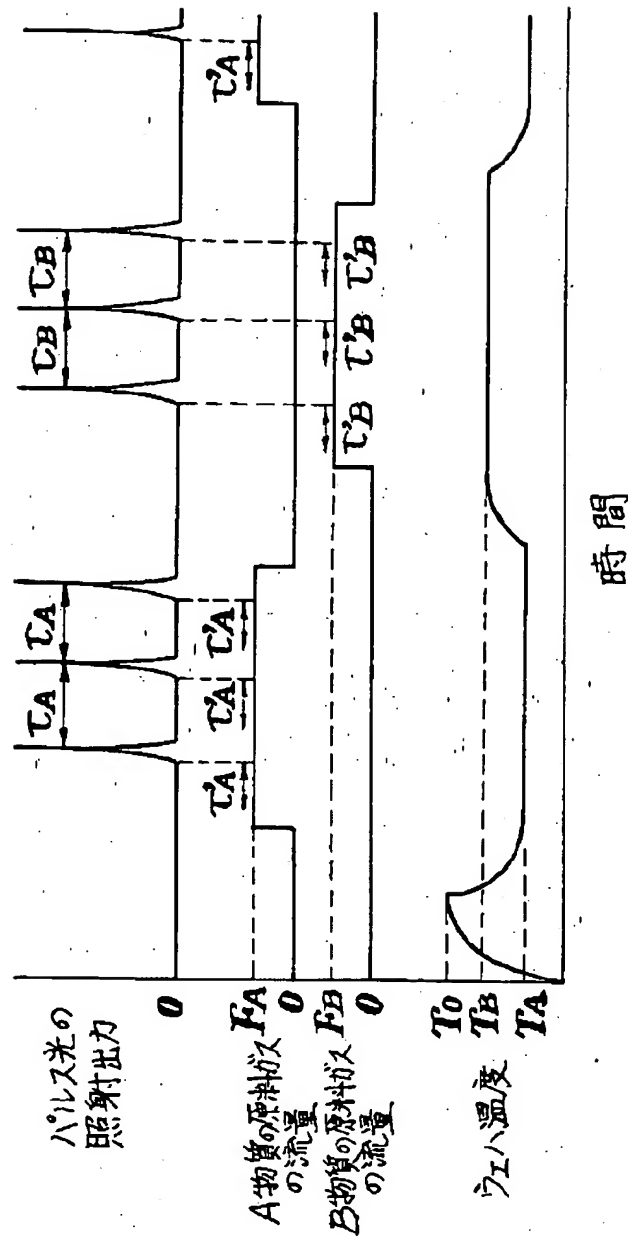
【図7】



【図9】



【図11】



フロントページの続き

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